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(54) PROCESS FOR THE PREPARATION OF A LUBRICATING OIL

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. formerly Shell Internationale Research Maatschappij N.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention is concerned with a process for the preparation of lubricating oil with a high viscosity index.

It has been found that lubricating oil with a high viscosity index can be prepared from high-boiling mineral oil fractions by converting the latter over a particular kind of boron-containing catalyst by means of hydrogen.

According to the present invention a process for the preparation of lubricating oil with a high viscosity index is characterised in that a high-boiling mineral oil fraction is contacted in the presence of hydrogen and at elevated temperature and pressure with a supported catalyst containing on an oxidic catalyst carrier (a) one or more of the metals iron, nickel and cobalt, and (b) one or more of the metals chromium, molybdenum and tungsten, and (c) boron.

It is important that boron be present as a catalytic component on the carrier, and for the avoidance of any doubt it is noted that the present invention does not include the use in the process just defined of a catalyst in which boron is only present in the material of which the carrier itself is formed.

For simplicity the metals iron, nickel and cobalt are frequently referred to hereinafter as iron group metals and the metal chromium, molybdenum and tungsten as Group VIB metals. References herinafter to a metal or metals of the iron group or a metal or metals of Group VIB of the Periodic Table of Elements should therefore be construed accordingly.

Suitable starting materials for the process according to the invention are mixtures of high-boiling hydrocarbons, for example heavy petroleum fractions and heavy fractions obtained by pyrolysis of coal, bituminous shale or tar sand. It is advantageous to use petroleum fractions boiling at least in part above the boiling range of lubricating oil. A very suitable feedstock for the present process is a fraction recovered by means of vacuum distillation from a petroleum residue obtained by atmospheric distillation. A vacuum distillate of this type has a boiling range which is usually between 350°C and 550°C. Particular preference is given, however, to deasphalted residual petroleum fractions.

The process according to the invention is carried out at elevated temperature and pressure and in the presence of hydrogen or a hydrogen-containing gas. Use may be made of pure hydrogen but this is not necessary. A gas with a hydrogen content of 70% by volume or more is perfectly suitable.

In practice, it will be preferred to use a hydrogen-containing gas originating from a catalytic reforming unit. Besides having a high hydrogen content, such a gas contains low-boiling hydrocarbons, such as methane, ethane and a small quantity of propane.

The temperature and pressure used in the present process may vary within very wide limits, depending on the desired degree of conversion. Advantageously, a temperature not lower than 350°C and not higher than

550°C will be selected. At temperatures below 350°C the rate of conversion decreases, whereas at temperatures above 550°C substantial cracking occurs so that only a limited quantity of the desired product is obtained. The preferred temperature is in the range from 400°C to 500°C. Pressures below 50 bar are unsuitable since they reduce the life of the catalyst and involve the risk of too high a content of aromatics in the product, as a result of which the viscosity index of the product would be adversely affected. A pressure above 250 bar would require very expensive equipment. It is preferred therefore to use a pressure lying in the 100 to 200 bar range.

The liquid hourly space velocity and the hydrogen/oil ratio may likewise be selected within very wide limits. It is preferred, however, to use a space velocity of between 0.1 and 10 kg of oil per hour per litre of catalyst. A space velocity of less than 0.1 kg/h.l. would require an uneconomically large reactor for a certain throughput, whereas at a space velocity of more than 10 kg/h.l. a low degree of conversion in the desired product would be obtained.

The preferred hydrogen/oil ratio is between 100 and 5000 standard litres (litres at 1 bar and 0°C) per kg of oil. At a very low H_2/oil ratio the life of the catalyst would be adversely affected, whereas at a very high H_2/oil ratio a large pressure loss would occur over the catalyst beds, necessitating much compression energy to circulate the hydrogen-rich gas.

The catalyst used in the process according to the invention contains on a carrier at least two hydrogenating metal components, and boron.

One of the metal components consists of at least one metal of the iron group or a compound of such a metal and moreover the catalyst should contain at least one metal of Group VIB or a compound of such a metal. Important factors in this connection are the quantity of the hydrogenating metal component, expressed as a percentage of the total catalyst, and the ratio of the metal of the iron group to the metal of Group VIB.

It is preferred not to use too small a quantity of metal component, since this could adversely affect the necessary hydrogenating action of the catalyst. If a very large quantity of metal component is incorporated, the pores of the porous catalyst carrier would become clogged so that part of the surface of the catalyst would be made inaccessible to the material to be converted. It has now been found that a catalyst containing 3—16% by weight of one or more metals of the iron group and 6—24% by weight of one or more metals of Group VIB is eminently suitable for the process according to the invention. For this reason the hydrogenating metal components are preferably applied to the catalyst in the said percentages by weight before using the catalyst for the present process.

The quantity of boron which is applied to the catalyst carrier may likewise vary within wide limits. It has been found, however, that the activity of the catalyst is dependent on the percentage by weight of boron present. A boron content of 1—20% by weight, calculated as B_2O_3, ensures good catalyst activity. It is therefore preferred to use a catalyst having such a boron content. Still better is a boron content of between 3 and 15% by weight, calculated as B_2O_3 in relation to the total catalyst, and it has been found that the maximum activity of the catalyst is obtained with a boron content of between 5 and 10% by weight, likewise calculated as B_2O_3 in relation to the total catalyst.

By activity as used in this specification is understood the temperature, which, under certain operating conditions (pressure, space velocity, H_2/oil ratio) and starting from a particular feedstock, is required to obtain a product with a predetermined viscosity index. The higher the activity of the catalyst used, the lower the temperature that is required. Although any metal of the iron group (iron, nickel, cobalt) and any metal of Group VIB of the Periodic Table of Elements (chromium, tungsten, molybdenum) is suitable for use as one of the two hydrogenating components of the catalyst for the conversion according to the invention, preference is generally accorded to a combination of nickel and molybdenum, as these produce the best results.

As carrier for the catalyst to be employed use can in principle be made of any oxidic refractory material. Suitable materials are, for example, alumina, silica, magnesia, titanium oxide and mixtures and compounds of these oxides.

It has now been found that catalysts with particularly good activity, selectivity and stability can be produced by using alumina as carrier material. The use of this carrier material is therefore preferred.

Commercially available alumina usually contains small quantities of impurities, such as silica and sodium. It has been found that alumina which contains 0.5—3% by weight of silica and not more than 0.005% by weight of sodium, is an excellent carrier material for the catalyst. This alumina is therefore preferred. If the alumina contains more than 0.005% by weight of sodium, the sodium content can be reduced to the desired percentage by means of ion exchange with an ammonium hydroxide solution.

In this context the selectivity of the catalyst is understood to mean the yield of lubricating oil with a certain viscosity index obtained when certain conditions (temperature,

pressure, space velocity, and H_2/oil ratio) are applied.

The stability of the catalyst is the extent to which it retains its activity on prolonged use in the process according to the invention.

To increase the activity and the selectivity of the catalyst further, fluorine and/or phosphorus is added thereto. It has been found that a considerable improvement is effected by the addition of as little as 1% by weight of fluorine and/or phosphorus. However, the addition of more than 6% by weight of fluorine and/or 12% by weight of phosphorus entails the risk of producing an adverse effect on the selectivity of the catalyst. It is therefore preferred to add 1—6% by weight of fluorine and/or 1—12% by weight of phosphorus to the catalyst.

The catalyst can be prepared in any manner desired, but preferably by impregnating the carrier with one or more aqueous solutions containing one or more components of one or more metals of the iron Group, one or more components of one or more metals of Group VIB of the Periodic Table of Elements and one or more boron components and by drying and calcination.

As stated previously, the catalyst used preferably contains on a carrier, nickel, molybdenum and boron. Such a catalyst can very suitably be prepared by impregnating a catalyst carrier with an aqueous solution of boric acid, drying the impregnating carrier and subsequently impregnating it with an aqueous solution of a molybdate and a nickel salt, whereupon the catalyst is completed by drying and calcination.

It has been found, however, that catalysts with very good activity, stability and selectivity can also be prepared by the successive addition of a nickel salt, a molybdate and boric acid to a hydrogel of a refractory oxide, preferably a hydrogel of aluminium hydroxide, whereupon the mixture is stirred, dried and calcined.

The preferred nickel salts are nickel hexamine dichloride ($[Ni(NH_3)_6]Cl_2$), nickel hexamine formate, nickel chloride and nickel nitrate although any water-soluble nickel salt, such as nickel formate, can be used.

The preferred molybdate is ammonium molybdate.

Boric acid and ammonium tetraborate are the preferred boron components.

After the addition of the metal components and the boric acid to the carrier, the mixture is stirred and dried. Stirring is preferably effected for 0.5—5 hours at a temperature between 10°C and 50°C. Drying is preferably effected at a temperature between 100°C and 150°C for 5—20 hours.

As stated previously, the catalyst should preferably contain fluorine and/or phosphorus. These elements can be applied to the catalyst by any convenient method. To this end the catalyst is preferably impregnated with a solution of phosphoric acid, phosphorous acid, ammonium phosphate, ammonium phosphite, hydrofluoric acid, ammonium fluoride and/or ammonium bifluoride. These components have the advantage that after calcination they do not leave behind on the catalyst unwanted cations such as sodium, potassium and calcium ions.

The catalyst is completed by calcination. The preferred temperature for this treatment is between 450°C and 850°C, over a period of 0.5—5 hours.

After calcination, the boron and the iron group and Group VIB metals are probably present in the catalyst in the oxidic form, although the possibility is not excluded that they may have combined, at least in part, with the catalyst carrier.

It has been found that in the catalytic conversion of heavy hydrocarbon mixtures into lubricating oil by means of hydrogen better results may be obtained by sulphiding the catalyst beforehand, during which the metal oxides are converted at least in part into the corresponding metal sulphides.

For this reason the catalyst is preferably used in the sulphided state.

A particularly good and therefore the preferred sulphiding method consists in contacting the catalyst—at a temperature of 250°C to 450°C, a pressure of 30—70 bar, a liquid hourly space velocity of 1—10 kg of oil per hour per litre of catalyst and a hydrogen/oil ratio of 50—500 litres (0°C and 1 bar) of H_2 per kg of oil—with an oil, preferably gas oil, which contains sulphur compounds. This treatment is preferably carried out in the same reactor vessel in which the hydrogenation conversion into lubricating oil takes place.

After sulphidation of the catalyst, the starting material for the production of lubricating oil with a high viscosity index is introduced into the reactor at a suitable temperature, pressure, space velocity and H_2/oil ratio, and passed over the catalyst, which is preferably present in one or more beds of particles whose size is between 0.5 and 5 mm.

After passing through the reactor, the reaction product is cooled and separated into a hydrogen-rich gas and a liquid product. It is preferred that at least part of the hydrogen-rich gas is recirculated to the reactor. The liquid product contains hydrocarbons boiling below the boiling range of lubricating oil and hydrocarbons boiling within the boiling range of lubricating oil. The hydrocarbons which boil below the boiling range of lubricating oil are separated from the higher-boiling residue, preferably by fractional distillation. The cut point of this distillation is preferably so selected that the higher-boiling residue has an initial boiling point in the range of from 350° to 450°C.

In addition to excellent lubricating oil components, this residue generally contains normal paraffins which solidify at ambient temperature and consequently have an unfavourable effect on the pour point of the lubricating oil. The use of the boron-containing catalyst has the great advantage that the residue contains considerably less normal paraffins than similar residues obtained by means of catalysts which do not contain boron. To produce a suitable lubricating oil or lubricating oil component from the residue it is nevertheless preferred to dewax this residue, albeit to a much lower degree than would be required if for the hydrogenative conversion of the starting material use was made of a catalyst which did not contain boron. This dewaxing treatment can be carried out in any manner desired. Dewaxing is preferably effected by means of a mixture of methyl ethyl ketone and toluene at a temperature between −10°C and −30°C and a solvent to oil volume ratio of between 1:1 and 10:1.

The dewaxed residue has a high viscosity index, for example, in the 100—140 range, depending on the conditions under which the hydrogenative conversion of the starting material takes place. For this reason it is eminently suitable for use as a "multigrade" lubricating oil or a "multigrade" lubricating oil component. This dewaxed residue can also be used to prepare, by vacuum distillation, one or more lubricating oils with high viscosity indices and varying viscosities, which oils may be further processed to produce excellent "multigrade" lubricating oils by mixing them with each other or with other components. The invention will now be further elucidated with reference to the following Examples.

EXAMPLE 1

Catalyst Preparation

A catalyst A, consisting of 71.0% by weight of Al_2O_3, 16.0% by weight of MoO_3, 8.0% by weight of NiO and 5.0% by weight of B_2O_3 was prepared by adding in succession nickel hexamine dichloride, ammonium para-molybdate and boric acid to an aluminium hydroxide hydrogel, stirring the mixture for 2 hours at room temperature, subsequently drying it for 12 hours at 120°C and calcining it for 2 hours at 650°C. After milling, the powdered catalyst was pelleted to pellets with a diameter of 3 mm.

A catalyst B, consisting of 70.0% by weight of Al_2O_3, 16.0% by weight of MoO_3, 8.0% by weight of NiO and 6.0% by weight of P_2O_5, was prepared by adding in succession nickel hexamine dichloride and ammonium para-molybdate to an aluminium hydroxide hydrogel, and after stirring for 2 hours at room temperature, phosphoric acid, whereupon the mixture was stirred for a further 30 minutes.

The mixture was subsequently dried for 12 hours at 120°C and calcined for 2 hours at 650°C.

After being reduced to powder the catalyst thus formed was pelleted to pellets with a diameter of 3 mm.

Lubricating Oil Preparation

Catalysts A and B were first sulphided for 36 hours by means of a heavy gas oil which contained 1.75% by weight of sulphur, under the following conditions:

temperature: 350°C
pressure: 50 bar
space velocity: 2 kg/l.h
hydrogen/oil ratio: 150 nl/kg

A residual oil fraction obtained from a North African crude, which oil fraction had been deasphalted by means of liquid propane, was used to test the activity, selectivity and stability of catalysts A and B.

This oil fraction had the following properties:

specific gravity: 20/4: 0.907
viscosity at 18°C: 32.8 cS
viscosity index (VI_E)* after dewaxing at −19°C: 77
yield of dewaxed oil after dewaxing at −19°C: 89.2% by wt

*) The viscosity index VI_E is determined by ASTM method D2270.

Quantities of this oil fraction were passed over two identical beds of catalysts A and B under the following reaction conditions:

pressure: 140 bar abs.
space velocity: 1 kg of oil per hour per litre of catalyst
hydrogen/oil ratio: 1000 litres (0°C and 1 bar) of H_2 per kg of oil.

During the catalytic conversions over the catalyst beds the temperatures were so adjusted that the products, after removal by distillation of components boiling below 375° C and after dewaxing, had a viscosity index (VI_E) of 120.

The dewaxing was effected by means of a mixture of methyl ethyl ketone and toluene (volume ratio 1/1) at a temperature of 127° C.

The following temperatures were required to produce the above result:

for catalyst A: 451°C
for catalyst B: 452°C.

These temperatures resulted in the following yields of dewaxed oil with a VI_E of 120 and an initial boiling point of 375°C,

expressed as percentages of the North African deasphalted residual oil fraction used as starting material:

for catalyst A: 32% by weight
for catalyst B: 35% by weight.

After components boiling below 375°C had been distilled off, the following quantities of paraffin wax, expressed as percentages of the North African deasphalted residual oil fraction used as starting material, were removed from the products of the hydrogenation conversions by dewaxing:

for catalyst A: 7% by weight
for catalyst B: 12% by weight.

From the foregoing it is clear that the boron-containing catalyst is almost as active and selective as the phosphorus-containing catalyst but that, if use is made of the boron-containing catalyst, the quantity of paraffin wax to be removed from the liquid product of the hydrogenation treatment is much smaller than if use is made of the phosphorus-containing catalyst to obtain a suitable lubricating oil. This is a major advantage since dewaxing is an expensive process.

Catalysts A and B both possess excellent stability. This was demonstrated by the fact that during the first 700 hours the temperature had to be raised by about 2°C every 100 hours to maintain the desired viscosity index, i.e. VI_E=120, while after 700 hours and up to completion of the experiments described above, i.e. 1100 hours, it was possible to keep the temperature constant and still achieve the desired result (VI_E=120).

EXAMPLE 2

A catalyst consisting of 66.5%wt Al_2O_3, 20%wt MoO_3, 6.5%wt NiO, 6%wt B_2O_3 and 1%wt F was prepared by impregnating dried alumina extrudates having a diameter of 1.5 mm with an aqueous solution of ammonium molybdate, nickel hexamine formate and boric acid.

The impregnated support was dried at 200°C and calcined during two hours at 500° C. The catalyst was then impregnated with an aqueous $NH_4H(F)_2$ solution and dried at 200°C and calcined during two hours at 500° C.

The catalyst was sulphided during 36 hours with the aid of heavy gas oil containing 1.75 %wt sulphur applying the following conditions:

temperature: 350°C
pressure: 50 bar
space velocity: 2 kg/h/l
hydrogen/oil ratio: 150 l (0°C, 1 bar) per kg.

A residual oil fraction obtained from a North African crude, which oil fraction had been deasphalted by means of liquid propane, was used to test the activity of the catalyst.

This oil fraction had the following properties:

specific gravity 20/4: 0.907
viscosity at 18°C: 32.8 cS
viscosity index $(VI)_E$ (ASTM-D2270) after dewaxing at −19°C: 77
yield of dewaxed oil after dewaxing at −19°C: 89.2 by wt.

The oil fraction is passed over a bed of the catalyst at the following reaction conditions:

temperature: 410°C
pressure: 140 bar absolute
space velocity: 0.8 kg/h/l
hydrogen/oil ratio: 1750 litres of H_2 (0°C, 1 bar) per kg of oil.

The liquid product of this treatment was separated by fractional distillation into a light fraction boiling below 400°C and a heavy fraction boiling above 400°C. The heavy fraction was dewaved with the aid of a mixture of methylethylketone and toluene (volume ratio 1/1) at a temperature of −27° C.

The produced quantity of lube oil after dewaxing was 33% by weight, calculated on the deasphalted residual oil feed.

The viscosity index (VI_E) of that oil was 124.

EXAMPLE 3

The experiment of example 2 was repeated with an identical catalyst and feed and under similar reaction conditions with exception of the reaction temperature which was 420°C. After dewaxing 23% by weight of lubricating oil having a viscosity index (VI_E) of 139 was obtained.

WHAT WE CLAIM IS:—

1. A process for the preparation of lubricating oil with a high viscosity index, characterised in that a high-boiling mineral oil fraction is contacted in the presence of hydrogen and at elevated temperature and pressure with a supported catalyst containing on an oxidic catalyst carrier (a) one or more of the metals iron, nickel and cobalt, and (b) one or more of the metals chromium, molybdenum and tungsten, and (c) boron.

2. A process according to claim 1, characterized in that the high-boiling mineral oil fraction is a vacuum distillate boiling between 350°C and 550°C.

3. A process according to claim 1, characterized in that the high-boiling mineral oil fraction is a deasphalted residual oil.

4. A process according to any one or more of claims 1—3, characterized in that use is made of a temperature between 400°C and 500°C, a pressure between 100 and 200 bar absolute, a liquid hourly space velocity between 0.1 and 10 kg of oil per hour per litre of catalyst and a hydrogen/oil ratio between 100 and 5000 litres of hydrogen (0°C and 1 bar) per kg of oil.

5. A process according to any one or more of claims 1—4, characterized in that the catalyst contains 3—16% by weight of one or more metals of the iron group.

6. A process according to any one or more of claims 1—5, characterized in that the catalyst contains 6—24% by weight of one or more metals of Group VIB.

7. A process according to any one or more of claims 1—6, characterized in that the catalyst contains 1—20% by weight of boron, calculated as B_2O_3.

8. A process according to claim 7, characterized in that the catalyst contains 3—15% by weight of boron, calculated as B_2O_3.

9. A process according to any one or more of claims 1—8, characterized in that the metal of the iron group is nickel.

10. A process according to any one or more of claims 1—9, characterized in that the Group VIB metal is molybdenum.

11. A process according to any one or more of claims 1—10, characterized in that the catalyst carrier consists wholly or substantially of alumina.

12. A process according to claim 11, characterized in that the alumina contains 0.5—3% by weight of silica and at most 0.005% by weight of sodium.

13. A process according to any one or more of claims 1—12, characterized in that use is made of a catalyst prepared by impregnating a dried catalyst carrier with one or more aqueous solutions containing one or more components of one or more metals of the iron group, one or more components of one or more metals of Group VIB of the Periodic Table of Elements and one or more boron components and by drying and calcining the impregnated carrier.

14. A process according to any one or more of claims 1—12, characterized in that use is made of a catalyst prepared by the successive addition of a nickel salt, a molybdate and boric acid to a catalyst carrier in the form of a hydrogel, whereupon the mixture is stirred, dried and calcined.

15. A process according to claim 13 or 14, characterized in that the iron group metal component used is nickel hexamine dichloride, nickel hexamine formate, nickel chloride or nickel nitrate.

16. A process according to any one or more of claims 13, 14 and 15, characterized in that the Group VIB metal component used is ammonium molybdate.

17. A process according to claim 13, characterized in that the boron component used is boric acid or ammonium tetraborate.

18. A process according to any one or more of claims 13—17, characterized in that drying is effected at a temperature between 100°C and 150°C for 5—20 hours.

19. A process according to any one or more of claims 1—18, characterized in that the catalyst contains 1—6% by weight of fluorine.

20. A process according to any one or more of claims 1—19, characterized in that the catalyst contains phosphorus.

21. A process according to any one or more of claims 1—20, characterized in that the catalyst contains 1—12% by weight of phosphorus.

22. A process according to any one or more of claims 1—21, characterized in that use is made of a sulphided catalyst.

23. A process according to claim 20, characterized in that the catalyst is sulphided by contacting it at a temperature between 250°C and 450°C and at a pressure between 30 and 70 bar absolute—the space velocity being 1—10kg oil per hour per litre of catalyst and the hydrogen/oil ratio 50—500 litres of hydrogen (0°C and 1 bar) per kg of oil—with an oil which contains sulphur compounds.

24. A process according to any one or more of claims 1—23, characterized in that hydrocarbons boiling below the 350°C to 400°C boiling range are removed by distillation of the product resulting from the catalytic hydrogenation treatment and that the higher-boiling residue is dewaxed.

25. A process according to claim 20, characterized in that the dewaxing is effected by means of a mixture of methyl ethyl ketone and toluene and at a temperature between −10°C and −30°C, the solvent to oil volume ratio being between 1:1 and 10:1.

26. A process for the preparation of a lubricating oil with a high viscosity index as claimed in claim 1, substantially as des-

cribed hereinbefore with special reference to the Examples.

27. Lubricating oils with a high viscosity index whenever obtained with the use of the process as claimed in any one of claims 1—26.

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